SYNOPSIS

Continuously diminishing fossil fuel resources, growing environmental concerns and changing geo-political scenario has incentivized the search for new energy resources and technologies. It has been well understood that future sustainable and green energy innovations will be mostly driven by the synthesis of new materials. Multicomponent high entropy oxides (HEOs) are perceived to serve as candidate materials in the field of catalysis, electro-chemical energy conversion and storage, electronic devices, thermal barrier coatings among many others. HEOs may be looked at as a recent vintage of the high entropy alloys (HEAs). They were brought into existence by innovative thinking with a dash of serendipity by Cantor and Yeh during 2004-05. HEOs were invented following the lineage of HEAs, however much later. The first HEO was reported in 2015 in CoCuMgNiZn-oxide by Rost et al. and was categorized as entropy stabilized oxide (ESO). Following this, a number of HEO systems have been reported. HEOs are slightly different than the HEAs as in HEOs there are more than one cation and anion sublattice and substitution may happen in either of them. The calculation of configurational entropy is also different in these systems. In addition, these systems are sensitive to environment in order to sustain their defect equilibria and electrical neutrality. It has been believed so far that all HEOs are single phase solid solutions with little or no reference to their stability.

The research work reported in this thesis has derived motivation to understand the formation of single-phase in rocksalt-, spinel-based HEOs and its derivatives, their stability and microstructural evolution. The thesis has been organized in seven chapters. **Chapter 1** introduces the basic concepts of designing HEOs, its similarities and differences with traditional dilute alloys, HEAs, bulk metallic glasses (BMGs) and their applications in the fields of catalysis, electrochemical energy storage and conversion. **Chapter 2** describes the

precursor metal oxides, heat treatment procedures for solid-state synthesis of multicomponent metal oxides and the working principles of the characterization techniques used.

Synthesis, phase evolution, composition modulation, local structural variation and their stability in multi-component equimolar (CaCoFeMgNi)-oxide and its ternary and quaternary derivatives have been reported in **Chapter 3**. The rationale behind synthesizing and characterizing the above material system as a starting point is the isostructuralism of all the constituent binary oxides in their +2 oxidation states. The empirical rules initially put forth for the formation of ESOs/HEOs by Rost et al., later by Sarkar and co-workers harp on non-isostructuralism of at least one constituent oxide, otherwise the 5-component mixture (HEO) shall inevitably end up being phase-pure with the same crystal structure as its constituent binary oxides. However, transition metals in their ionic states are known to display multiple oxidation states. Oxygen partial pressure is also known to alter the oxygen stoichiometry in metallic oxides leading to an anion deficient or excess composition, which in turn produces various kinds of defect microstructures. It was found out that the ternary equimolar (CoMgNi)-oxide exhibited single-phase signature from X-ray diffraction (XRD) experiments, while quaternary equimolar (CaCoMgNi)-oxide produced a two-phase mixture, both having the cubic rocksalt structure, however one rich in Co-, Mg-, Ni-ions (major phase, ~62%, a=4.15Å) and the other rich in Ca-ions (minor phase, ~38%, a=4.83Å). The equimolar (CaCoFeMgNi) multicomponent oxide (MCO) showed a complex diffraction pattern which could be indexed to the presence of at least four phases. The major rocksalt phase enriched in (Co,Mg,Ni), forms almost 50% of the phase fraction while Fe-enriched ordered hexagonal phase forms ~35% and the remaining Ca-enriched regions form a rocksalt phase (a=4.83Å) as well as a spinel phase (a=8.32Å), with combined phase fraction of around 15%. SEM-XEDS chemical mapping clearly brings

about large-scale chemical segregation of Ca- and Fe-ions, however, maintaining the presence of all five cations in all the phases but to varying extents. Transmission electron microscopy (TEM) results throw insight into the phase formation, its stability and microstructural evolution after sintering at 1473K for 10h as well as for 100h followed by water quenching. The system tries to reduce the lattice strain arising out of the major phase (Co, Mg, Ni enriched rocksalt) by systematic mutual in-plane and out-of-plane rotation amongst the structural domains forming a helical structure. This leads to the appearance of linear fringes having alternating contrast with 2-5 nm width in diffraction contrast imaging along with extensive spot-splitting and arcing of spots in the single crystal diffraction patterns. The Fe-rich hexagonal phase on the other hand undergoes structural ordering with cations and vacancies producing anti-phase domain boundaries in the process, along with array of fine twin-related planar faults which grows significantly with prolonged exposure at high temperatures. Furthermore, there are also some regions within the MCO where three phases having cubic rocksalt, cubic spinel and ordered hexagonal structures are found to co-exist. They possess a definite orientation relationship among them with coherent/semi-coherent interphase interfaces.

The first ever reported (CoCuMgNiZn) ESO has been taken up as the model system, and the exploration of its physical metallurgy is given in **Chapter 4**. X-ray diffraction (XRD) studies indicate that the HEO is single phase with cubic rocksalt structure on average. However, XRD pattern obtained from the sintered pellets and powder shows systematic shoulders associated with all the fundamental peaks of rocksalt phase (a~4.23Å) along with a reversal of intensities of the first two peaks having non-ideal intensity ratio. Upon peak deconvolution, signatures from constituent oxides of CoO, MgO and NiO brings out an excellent match with the reported d-spacings. In the hyperspectral chemical mapping (SEM-XEDS), fine-scale segregation of Mg- and Cu-ions could be discerned, which

becomes more prominent with prolonged exposure at elevated temperature. TEM BF-CDF imaging along with corresponding SAED pattern from z=[100] zone axis of the sintered and quenched quinary HEO exhibit wavy domain like structure of alternating contrast with diffused interfaces oriented along the <002> directions of the cubic rocksalt structure. Moreover, geometric shape evolution of the diffraction spots could be discerned along with diffuse streaking between it. Such a diffraction pattern translates into mutually rotated cubic domains, occasionally with a hint of tetragonality, that prefers to grow along the c-axis of the FCC crystal structure in 3-D. The tweed morphology as viewed from the four-fold axis of the cubic rocksalt structure, appears as discontinuous jagged steps of alternating contrast from the z=[011] zone axis. The tweeds, with minor chemical fluctuations, may act as template for enhanced phase separation to produce a self-assembled microstructure, provided sufficient stimulus is applied to overcome its kinetics of solid-state phase transformation. The HEO was subsequently aged at an intermediate temperature of 723K for 120h to understand its phase stability and microstructural evolution. Although the quinary HEO maintains its global average rocksalt structure, as understood from the XRD pattern, however with major peak broadening and highly non-ideal peak ratios. This observation is counterintuitive as the system gets more time to relieve its residual strain. TEM imaging clearly reveals grown domain structure, however not grown to a large extent, in-line with the anticipated sluggish kinetics of the material system. The domain interior is of lighter contrast while the domain walls are of darker contrast, with occasional appearance of δ-fringe contrast. These evidences point to the metastability in the time-temperature space of the phase-pure quinary composition with respect to systematic structural modulation accompanied by minor composition fluctuation. Furthermore, in a bid to release its volumetric strain, apart from lattice strain, arising from the multi-cationic sublattice, a cubic spinel phase (double the lattice parameter) is found to coexist with cubic

rocksalt phase having a definite orientation relationship and sharing perfectly coherent interfaces. To the best of knowledge of the author, such direct observations and inferences have not been reported in literature during the last decade, following the discovery of the first HEO having rocksalt crystal structure in 2015.

Chapter 5 encompasses the effect of systematic partial substitution of cations in equimolar ratio on the phase evolution, its stability and microstructural formation. Equimolar ternary (CoMgNi)-oxide, common to both the previous chapters, has been explored thoroughly. The as-mixed mixture produced signatures from both rocksalt (CoO, MgO, NiO) and spinel (Co_3O_4) phase. However, with the advent of progressive high-energy ball-milling, a competition between the two phases could be seen in the form of peak mergers. Apart from that, the shift of peaks with higher h of milling was found to be non-unidirectional, which is counterintuitive. The competing shifts of the peaks may be attributed to combined phenomenon of build-up of varying amount of vacancy concentration in both the phases upon milling, with refinement of particle size and concomitant increase in lattice strain. Upon sintering and quenching, the equimolar ternary composition exhibits phase-pure signature of a disordered rocksalt phase (a~4.2Å). However, the sintered pellet shows a sharp (220) peak of a spinel phase (a=8.36Å), which was only seen as a hump for the sintered powder. It becomes evident after analysis that the crushing action of the sintered pellet (owing to the brittle nature of ceramics) increases the strain in the material, which in turn raises the Compton modified background, enabling it to mask low intensity peaks from structurally correlated phases having low phase fractions. TEM observations could not find conclusive evidence for coexisting spinel phase owing to its rather small volume fraction. However, upon ageing the sintered (CoMgNi)-oxide at intermediate temperature for long h, extensive fringe contrast of 1.5-3.5 nm width could be seen in the micrographs along with major spot-splitting and arcing in the corresponding diffraction patterns. Several

intensity maxima could be deconvoluted from each principle spot of the z=[001] zone axis pattern, which could be systematically joined to obtain several four-fold symmetry shapes that are rotated with respect to each other. Partial substitution by Mn- and Fe-ions in equimolar (CoMgNi)-oxide resulted in phase-pure spinel (a~8.38Å) signature from the sintered and quenched quinary (CoFeMgMnNi)-oxide. This HEO forming composition has not been reported before. However, the peaks in the XRD pattern are finitely broad with non-uniform intensity ratios along with shoulders and splits, especially in the peaks of (222), (400) and (440). It could simultaneously be indexed to (111), (200) and (220) planes of a rocksalt phase with half the lattice parameter. This single-phase spinel-forming composition was further sintered at elevated temperature for prolonged time to check the phase stability, which resulted in a very similar diffraction pattern as the sintered and quenched one. However, electron diffraction and TEM imaging points at a nuanced picture in the energy landscape of the HEO, which was previously unanticipated. Systematic presence of fringe contrast along with domain-like morphology from two major zone-axes of the spinel structure reveal systematic presence of other spots. Those spots may be indexed to a rocksalt phase of exactly half the lattice parameter of the spinel phase, which are found to be have definite orientation relationships with each other. The interface structure is mostly semi-coherent. It may be inferred that rocksalt domains grow locally inside the major spinel phase, and vice-versa as proved in the previous chapter, all in a bid to relieve the geometric frustration in the lattice. Furthermore, Mg- was replaced by Cr-ions to synthesize (CoCrFeMnNi)-oxide, the first reported spinel forming HEO. Although the XRD pattern brings out a high degree of one-to-one correspondence as obtained from (CoFeMgMnNi)-oxide, however with peak broadening and excessive shouldering. TEM BF-CDF imaging interestingly reveals interweaved domain-like morphology of 5nmx5nm with alternate dark and bright contrast. Corresponding electron diffraction pattern from

z=[001] zone axis exhibits continuous diffuse streaking along mutually perpendicular <220> directions. This points to coordinated local structural modulation assisted phase separation event, although at the nascent stage in the spinel HEO, which was unanticipated since its discovery.

Chapter 6 documents structure-property correlation of all the MCOs/ESOs/HEOs explored in the previous experimental chapters. Since this class of materials have multi-faceted areas of application owing to its favourable functional properties in general, the performance of them as catalysts for efficient evolution of oxygen and hydrogen from electrochemical water-splitting experiments has been carried out. Using a three-electrode setup, all the equimolar ternary, quaternary and quinary MCO/ESO/HEO compositions were tested against linear sweep voltammetry (LSV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests. It was found out for apparent phase-pure compositions, the catalytic performance drops consistently with ageing in the all the cases. Such an observation could be attributed to the fine-scale segregation of redox active Co-, Cu-, Fe- Ni-, Mn-ions as observed from SEM-XEDS chemical mapping. Moreover, multi-phasic (CaCoFeMgNi)-oxide produces the least promising dataset, while the two-phase mixture of rocksalt and spinel phases in equimolar (CoMgMnNi)-oxide outperforms all the other compositions, with the lowest overpotential of 390 mV at a current density of 10mA/cm^2 and lowest Taffel slope of ~74.6 mV/dec. Such an observation hints to enhanced electrocatalytic performance where reversible inter-conversion between two related phases may occur during oxidation and reduction cycles of the water-splitting process. It further validates the school of thought put forth by Zhai et al., on the use of poly-cationic oxides (PCOs) for efficient two-step thermochemical water-splitting.

Chapter 7 discusses the major conclusions arising from the research work carried out throughout this thesis as a whole, along with a few points for future scope of exploration.